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I–V CHARACTERISTICS OF IONIZED CLUSTER BEAM DEPOSITED Ag/n-Si(111) SCHOTTKY DIODE

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Temperature dependence of the effective Schottky barrier heights, ϕ_b and the relevant ideality factors, n, deduced from the I–V measurements of the ionized cluster beam, deposited Ag/n-Si(111) structures as a function of the ionized silver atoms acceleration voltage, U_a, were investigated. The observed large differences in the diode saturated reverse current as a function of U_a are interpreted on the basis of the thermionic field emission theory of major charge carrier transport. It is, however, established that the theory can not satisfactory predict our I–V temperature dependent measurements. The qualitative interpretation of measurements is presented, which is based on the proposed conjectured charge carriers energy band diagram. A hypothesis is forwarded that, in addition to the regular Ag/Si Schottky potential barrier, another potential barrier appears at a presumably assumed abrupt interface within the Si wafer, which divides the Ag^+ enriched region from the regular n-doped Si depletion region. This barrier affects considerably the shapes of valence and conducting semiconductor energy bands, which may undergo a continuous displacement. The magnitude of the band shift is expected to be an increasing function of the silver dopants density and of their penetration lengths. It is proposed that for $U_a \neq 0$, the charge carrier transport is in ICB deposited structures, governed by the regular thermionic field emission of electrons tunnelling through the metal semiconductor barrier, enhanced by the simultaneous charge

carriers diffusion arising on account of the multiple-level recombination processes. This current is, presumably, taking place in the vicinity of the above described additional interface, which likely constitutes a strong asymmetrical p-n junction.

1. *Introduction*

Formation of thin films of various electrical, magnetic, and even organic substances on suitably chosen substrata is, among numerous other well established methods, conveniently accomplished by Takagi [1,2] ionized cluster beam, (ICB), vacuum deposition.

The essential idea of the ICB deposition method is illustrated in Fig. 1. The material to be deposited is evaporated in a closed crucible with a small nozzle on top. The vapours, while escaping through the nozzle, undergo adiabatic, supersonic expansion and during this process some of the atoms may reportedly [2] aggregate in clusters of up to a few dozen or more atoms. The jet of atoms and atomic clusters is subjected to electron impact ionization. Ionized particles, on their path towards the substrate, are accelerated in the static electric field. In general, the ejected atoms or clusters are singly positively ionized in a large proportion.

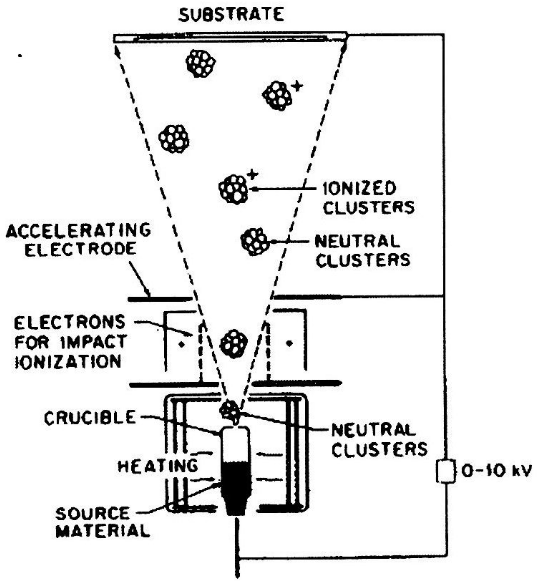


Fig. 1. Schematic drawing of an ion cluster beam deposition experiment [2].

It has been generally agreed [1,2] that by the ICB deposition method, being a low temperature thin film growth process, a very good quality thin films are produced. The reason is attributed to the still unknown effects which accompany this particular ion assisted method of thin film deposition. Known are at least two additional important features contributing to the high quality thin film growth, namely the fact that there are no extra atomic species which could contaminate or be incorporated in the film growing process and the observation that the amount of damage on the substrate due to the impinging particles, depending on the experimental condition, may be very small indeed.

The potential barrier height, ϕ_b, as derived from I–V measurements, of conventionally UHV deposited Ag/n-Si(111) Schottky diode, is reported to be 0.68 eV [3]. However, when deposited by the ICB, deposition method [1], depending on the value of the experimental parameter the ionized cluster acceleration voltage U_a, the apparent potential barrier height of the structure above can be tailored to vanish. By a proper choice of the ionized cluster acceleration voltage, the silver ions acquire a kinetic energy that is sufficient to penetrate the Si substrate.

It is the purpose of the present paper to provide a quantitative conjecture of the physical process that is considered the cause for the described properties.

2. Sample preparation

Ag/n-Si(111) Schottky diodes were prepared by the ICB deposition of silver onto the polished surface of (111) silicon wafer of electrical resistivity $\rho = 0.5$ Ωcm and P doped density of 10^{16} cm^{-3}. Before deposition, the wafer was subjected to the wet cleaning and passivization procedure described in Refs. 4 ad 5. It is a well established fact [5] that the Si wafer, following the surface preparation, is (under the normal laboratory atmospheric conditions) almost immediately covered by an extremely stable (for the period of up to one year) dielectric thin film consisting of about 0.7 nm thick native oxide planar layer with an about 0.2 nm thick organic contamination layer on the top.

The investigated Ag/n-Si(111) diodes were deposited under identical conditions except for the acceleration voltage of ionized silver clusters which were chosen to be $U_a = 0$, 300 and 1000 V, respectively. Vacuum pressure inside the chamber was 10^{-3} Pa, cluster ionization current was 50 mA, the deposition rate was approximately 1 nm/s and the Si(111) wafers were held at temperatures bellow 423 K (150 °C). The thickness of the deposited Ag thin films were measured to be about 200 nm on the front side and about 400 nm on the back side of the Si wafer.

It is important to note that the ohmic contacts on the back sides of the Si(111) wafers were accomplished by the identical deposition of silver metal as at the front side. However, the acceleration voltage was large, say $U_a = 6$ kV. Thus, apart from the cleaning and passivization, the Si(111) wafers were not subjected to any other technological treatment.

3. I–V measurements

I–V characteristics were measured using the "KEITHLEY 236 Source Measure Unit". They were recorded in the temperature interval from 150 K to 300 K. The room temperature I–V characteristics of Ag/n-Si(111) Schottky diodes, for $U_a = 0$ V, 300 V, and 1 kV, are presented on Fig. 2. The diameter of diodes was 1mm.

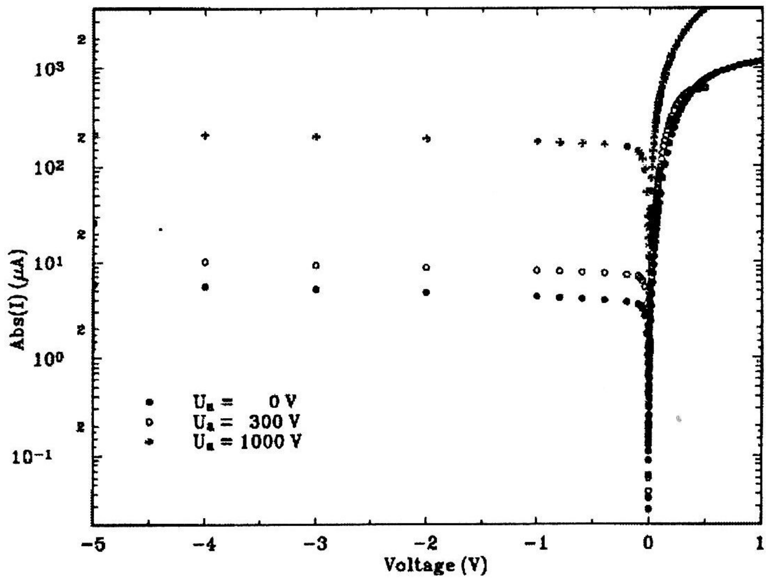


Fig. 2. Room temperature I-V characteristics of Ag/n-Si(111) *Schottky diodes deposited for three different acceleration voltages,* U_a.

As evidenced in Fig. 2, the reverse current seems to be saturated in all three cases. This is an indication that either the thermionic emission, or the thermionic field emission [6] is the dominant current transport mechanism in the above samples. Figure 2 suggests that, whatever the yet to be discovered physical process is responsible for Schottky barrier formation, the effect of the increasing ICB acceleration voltage, U_a, appears to lower the apparent height of the Schottky potential barrier. The obvious most important singular factor affecting the observed behaviour appears to be the penetration of Ag ions into the Si substrate. The penetration lengths, assuming that the surface of Si substrate is covered by the 1.1 nm thick SiO_2 layer, were calculated by the computer program TRIM-90 [7], using the calculated stopping ranges of single Ag ions, L. For the cases of our interest at: $U_a = 300$ V, $L = 2.4$ nm, $U_a = 1$ kV, $L = 4.0$ nm, and $U_a = 6$ kV, $L = 9.2$ nm.

On account of what appears to be the strong Si semiconductor doping (for $U_a = 0.3$ kV and 1 kV) beneath its surface, the experiment was analyzed assuming the thermally assisted tunnelling of electrons (thermionic field emission current) as the dominant current transport. The reason is that the tunnelling theory [6] can account for the lowering of the *effective* potential metal/semiconductor barrier as a function of doping. Consequently, we attempted to interpret the *reverse* biased I–V characteristics on the basis of the expressions [6] (valid for $V_r > 3kT/q$),

$$J = J_s e^{-(\phi_b/E_0 - V_r/E^{'})} = J_s e^{-q\phi_{eff}/kT}, \tag{1}$$

where J is the measured current density, V_r is the reverse voltage and J_s is the saturation current density as defined below. In Eq. (1), ϕ_b is the "true" potential barrier height which is related to the effective potential barrier, ϕ_{eff}, by the definition above, E_0, and $E^{'}$ are parameters defined by

$$E_0 = E_{\hat{0}\hat{0}} \coth\left(\frac{qE_{\hat{0}\hat{0}}}{kT}\right), \quad E^{'} = \frac{E_{\hat{0}\hat{0}}}{[(qE_{\hat{0}\hat{0}}/kT) - \tanh(qE_{\hat{0}\hat{0}}/kT)]} \tag{2}$$

and $E_{\hat{0}\hat{0}} = \sqrt{h(N_d/m_*\epsilon_s)}/4$. Here T is the temperature, k is the Boltzmann's constant, q the electronic charge, N_d the donor density, m_* the electron effective mass, $\epsilon_s = \epsilon\epsilon_0$, and h is the Planck's constant. The term J_s depends on the reverse voltage, V_r, and is defined as

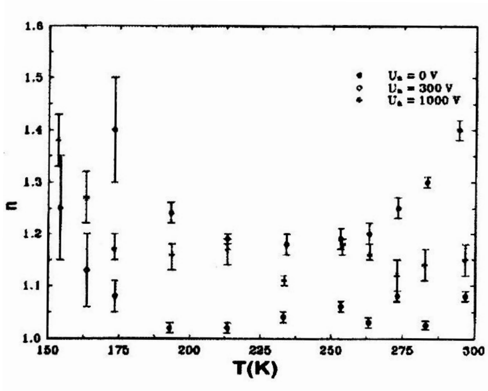
$$J_s = \frac{A^*T\sqrt{\pi qE_{\hat{0}\hat{0}}[q(V_r - \zeta) + q\phi_b/\cosh^2(qE_{\hat{0}\hat{0}}/kT)]}}{k} \tag{3}$$

where, A^* is the Richardson constant for the metal and $q\zeta(= E_c - E_F^s)$ is the energy as measured from the Fermi level to the semiconductor conduction band. It is to be noted that the expressions above are, in general, predicting the following:

1) The effective Schottky barrier height decreases linearly with increasing reverse bias (under appropriate conditions, providing the tunnelling current predominates), and/or

2) that the increased semiconductor doping lowers the effective barrier defined by the expression $\phi_{eff} = kT(\phi_b/E_0 - V_r/E^{'})/q$. This effect arises because the width of the tunnelling potential barriers narrows with the increased semiconductor doping density.

The temperature variation of the "effective" barrier height, ϕ_b, and the ideality factor, n, (defined as $n = (q/kT)\partial V/\partial(\ln J)$, Ref. 3) as determined from expressions above, are presented in Figs. 3 and 4. It was necessary to take into account the parallel, R_p, and series resistances, R_s, of our structures which were found to be (at the room temperature): $R_p = 2.6$, 1.5, and 0.1 MΩ and $R_s = 510$, 280 and 83 Ω, for $U_a = 0$, 300 and 1000 V samples, respectively. The derived barrier heights are monotonicaly decreasing functions of temperature. However the ideality factor, n, shows more complicated behaviour, and can not be described in terms of the T_0 factor, i.e. $n \neq 1 + T_0/T$, [6]. The parameters qE_∞, as obtained in the fitting, depending on the acceleration voltage, are always less than kT, and vary from about 2 meV at room temperature to about 12 meV at the lowest temperature investigated. As the donor density is proportional to E_∞^2, this functional dependence is just the opposite of what is expected. Consequently, the thermionic emission theory of Ref. 6, which could possibly reflect the major feature of the experiments (presumably a changing density of fixed charge carriers in the sample), fails to predict the temperature variation of our ICB deposited structures.



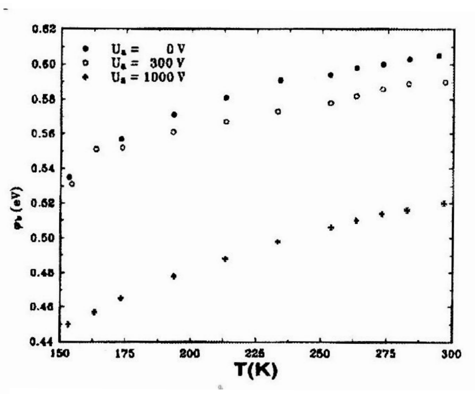


Fig. 3. Temperature dependence of heights barrier of ICB deposited Ag/n-Si *Schottky diodes, as obtained from I–V measurements.*

Fig. 4. Temperature dependence of the ideality factor, n, of ICB deposited Ag/n-Si(111) *structures (right).*

In fact, this conclusion is supported by considering our recent explicit calculations of the electron quantum mechanical tunnelling through heavily doped triangular potential barrier [8]. The results yield to low current densities for any reasonable value of Ag^+ doping density and its penetration range as parameters. However, the reverse current does exhibit the correct dependence on doping density.

In the limit when $kT \gg qE_\infty$ (not the case above), it follows that $E_0 = kT/q$, and the current density, J, as given by Eq. (1) above, reduces to the well–known equation for the reverse current of the thermionic emission process of majority of the carriers current transport [3].

4. Results and discussion

The drastic changes seen in the reverse part of the I–V diagram are usually attributed to the so–called leakage current, an effect presumably related to the strong electric field at the edge of the diode. In the reported cases above, the surfaces of diodes were all equal (of diameter 1 mm), consequently the observed differences, to a large degree, reflect the events associated with the penetration of Ag ions into the Si substrate. As is well–known, Ag does not form a silicide compound.

We propose that the I–V measurements, as described above, could be understood on the basis of the following model. It is to be noted that $U_a = 0$ case represents an example of a conventional Schottky barrier with a thin oxide interface layer between the metal and semiconductor. It served as a "standard" and the other two ICB reported experiments were compared to it.

The $U_a \neq 0$ structures represent, however, an essentially different situation. The I–V measurements (Fig. 2) with our ICB deposited Ag/n-Si(111) Schottky diodes could be consistently explained invoking the assumption that the distribution of Ag ions within the Si substrate is uniform up to their stopping lengths. As previously discussed, the stopping length is a function of U_a, and though the Ag penetration range distribution within Si is expected to be very complicated, we assume Ag ions to be, in the first approximation, uniformly arranged throughout the Si region up to the, U_a dependent, (abrupt) penetration depth. This is an important observation based on the experimental facts [2]: a) that the translational velocity of a single Ag atom from the 1mm diameter nozzle is about 600 m/s (kinetic energy is 0.2 eV), and b) that, on account of *various* sizes of clusters present in the beam, the translational energy of a particular cluster of Ag atoms (which disintegrates upon impact) is given by the above value divided by the number of Ag atoms in a cluster. It follows, that the maximum Ag penetration range is determined by the acceleration voltage of a single, from the nozzle ejected Ag^+ ions, and the penetration lengths of others are inversely proportional to the number of cluster constituents.

The Ag impurity in Si is reported [3] to occupy the *donor* energy level at 0.37 eV above the valence band, although it also may occupy an *acceptor* level at 0.72 eV above E_V. Consequently, the Fermi energy of the Ag donor enriched (likely polycrystalline) region of the Si substrate increases and may become even degenerate under favourable conditions. The requirement that in the equilibrium Fermi levels of the three different regions (silver metal, Ag^+ enriched n-Si region, and n-Si semiconductor region) ought to be equal, induces band bending at the (assumed) abrupt Si plane, akin the usual p-n semiconductor band bending situation. The Ag enriched (additionally donor doped) Si region is, consequently, downshifted in energy with respect to the n-Si energy bands. According to the proposed conjecture, it is possible to understand our experimental I–V results on the basis of the energy band diagram shown in Fig. 5, as due to a particular case of simultaneous processes of thermally assisted electron tunnelling through the Schottky potential barrier and the diffusion governed charge carrier transport at the newly induced, abrupt, strongly asymmetrical p-n potential barrier within the semiconductor.

The magnitude of the band shift is expected to be an increasing function of the silver dopant density and their penetration lengths, respectively. Increasing U_a, results in a denser and wider Ag enriched donor region, consequently E_c band minimum is lowered and the metal/Ag-Si enriched region becomes correspondingly thinner. However, the asymmetric p-n barrier increases instead. All this results in an increased tunnelling electron yield (at a fixed value of the reverse voltage and constant temperature) through the metal/semiconductor contact, enhanced by the hole current at p-n junction, arising on account of the multiple-level recombination processes in Ag^+ enriched region, in agreement with the I–V observations. An indirect evidence for the existence of such centres is provided by the AES depth profiling analyses (not shown), exhibiting C, N, S and O impurities in such Ag^+

enriched region, respectively.

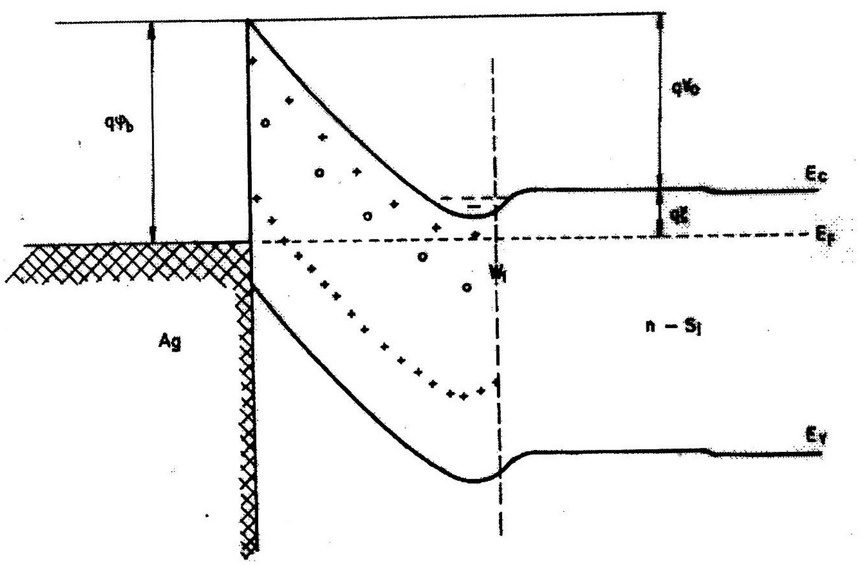


Fig. 5. Conjectured, equilibrium (V=0) charge carriers energy band diagram, for ICB deposited Ag/n-Si(111) *structures deposited for non–zero value of the cluster ions acceleration voltage.*

The proposed model is also supported by the measured temperature dependence of the reverse current for $U_a \neq 0$ structures (not shown), where a drastic decrease of the reverse current (but only for these structures) with decreasing temperature has been observed. As is known, this behaviour is typically associated with the diffusion processes only.

As indicated above, the conjectured band bending model provides results which quantitatively agree with the I–V measurements of IBC deposited Ag/n-Si(111) Schottky barrier structures. However, its detailed experimental and theoretical verification and the possible applications must be subjects of future investigations.

5. Conclusions

The temperature dependence of the effective Schottky barrier heights, ϕ_b, and the relevant ideality factors, n, deduced from the I–V measurements of the ionized cluster beam deposited Ag/n-Si(111) structures as a function of the ionized silver atoms acceleration voltage, U_a, are presented. It has been shown that the thermionic field emission theory of major charge carrier can not account for the observed large differences of the diode I–V temperature dependent measurements as a function of U_a.

The qualitative interpretation of measurements is presented. It is based on the proposed charge carriers energy band diagram. A hypothesis is forwarded that, besides the presence of the regular Ag/Si Schottky potential barrier, another potential barrier occurs at an additional, presumably abrupt, interface within the Si wafer, which divides the Ag^+ enriched region from the regular n-doped Si depletion region. This barrier considerably affects the shapes of valence and conducting semiconductor energy bands, which may undergo a continuous displacement. The magnitude of the band shift is expected to be an increasing function of the density of silver dopants and of their penetration lengths. It is proposed that the charge carrier transport in ICB deposited structures, for $U_a \neq 0$, is governed by the regular thermionic field emission of electrons tunnelling through the metal semiconductor barrier, enhanced by the simultaneous charge carrier diffusion arising on account of the multiple-level recombination processes. This current is presumably taking place in the vicinity of the above described additional interface, which likely constitutes a strong asymmetrical p-n junction.

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$I-V$ KARAKTERISTIKE Ag/n-Si(111) SCHOTTKYJEVE DIODE NAČINJENE POMOĆU IONIZIRANOG SNOPA NAKUPINA

Istraživana je temperaturna ovisnost efektivne visine Schottkyjeve barijere, ϕ_b, i faktora idealnosti, n, analizom $I-V$ mjerenja sa Ag/n-Si(111) strukturama, postignutim nanošenjem ioniziranih nakupina Ag atoma, u ovisnosti o naponu ubrzanja nakupina. Izložena je hipoteza da se pored redovne Ag/Si Schottkyjeve barijere javlja druga potencijalna barijera, vjerojatno na pretpostavljenoj oštroj granici unutar Si pločice, koja dijeli područje obogaćeno sa Ag^+ od osiromašenog područja n-Si. Smatra se da prijenos naboja za $U_a \neq 0$ upravlja pravilna termionska emisija elektrona koji tuneliraju kroz barijeru metal-poluvodič, pojačana difuzijom nositelja naboja preko višerazinskih rekombinacijskih procesa.